

JAPANESE

[JP,05-140386,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL
FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention is excellent in ductility, gas barrier property, hot water resistance, oil resistance, shock resistance, etc. which serve as an ethylene-vinylacetate copolymer partial saponification thing from terminal modification polyamide resin, and relates to a resin composition suitable for carrying out continuous molding especially of the wrapping.

[0002]

[Description of the Prior Art]Since an ethylene-vinylacetate copolymer partial saponification thing (it omits the following EVOH) excels [permeability / oxygen] in oil resistance very small and transparent mold goods are moreover easily obtained by the usual melt molding

processing method. It is especially useful as wrapping, such as a film, a sheet, a tube, and a plastic container. On the other hand, by that the transmissivity of moisture lacks in hot water resistance greatly since EVOH is hydrophilic nature, and stiffness, since there are faults, like that impact strength is easily small and ductility is very bad, use expansion is restricted.

[0003]the method of mixing polyamide to EVOH is proposed as one of the means which improves the fault of such EVOH conventionally (JP,44-24277,B.) It is known that impact strength will be improved holding the gas barrier property which is the feature of EVOH and good transparency, and oil resistance according to JP,48-22833,B, JP,50-121347,A, and this method.

[0004]

[Problem(s) to be Solved by the Invention]Although the constituent which consists of EVOH and polyamide demonstrates many desirable characteristics extremely as wrapping and the high mold goods of commodity value are obtained, a serious fault exists actually. if EVOH and polyamide are mixed by a molten state, both will cause a chemical reaction, as a result, the viscosity of a mixed composition increases, and it results in gelling with intense coloring -- it comes out rattlingly.

[0005]That is, the constituent which benefits this disadvantageous phenomenon from EVOH and polyamide cannot apply the continuous manufacturing process of practical use products, such as a film, a sheet, and a tube, with difficult continuous molding.

[0006]Although the method of improving continuous molding nature when a terminal carboxyl group uses little polyamide of what is called amino-terminus Rich with many terminal amino groups as polyamide is shown in JP,62-13449,A and JP,62-106944,A as this measure, It is difficult to prevent gelling thoroughly also by these methods, and to be able to perform continuous molding over a long period of time further is desired.

[0007]Then, this invention persons hold the EVOH improvement effect which polyamide has, And as a result of inquiring wholeheartedly in order to obtain the resin composition which does not present the increase in viscosity at the time of melting as EVOH and a polyamide mixture show, by using the polyamide which denaturalized the

amino terminal as polyamide blended with EVOH, it found out that the above-mentioned purpose could be attained and this invention was reached.

[0008]

[Means for Solving the Problem] Namely, content of this invention of (a) ethylene-vinylacetate copolymer partial saponification thing 1 - 99 % of the weight and the (b) terminal amino group is 3.0×10^{-5} Eq/g or less, And a thermoplastic resin composition, wherein relative viscosity [eta] of polymer consists of 99 to 1 % of the weight of terminal modification polyamide resin which is 2.0-7.0 is provided.

[0009] As for EVOH used by this invention, not less than 90% of the degree of ethylene content % and saponification of 10-60 mol is an ethylene-vinylacetate copolymer partial saponification thing of not less than 95% of the degree of ethylene content % and saponification of 20-50 mol preferably. Since it is easy to color when EVOH below 10 mol % is inferior in melt extruding nature and an ethylene content fuses a constituent with polyamide, and it is moreover easy to carry out a pyrolysis, it is not desirable. On the other hand, although the melt extruding nature of a constituent is good, gas barrier property is inferior in EVOH in which an ethylene content exceeds 60-mol %. Since gas barrier property also falls to a degree very much while less than 90% of EVOH lacking in the dimensional stability of mold goods and becoming easy to carry out heat contraction of the degree of saponification, it is not desirable.

[0010] Although there is no restriction in particular about a degree of polymerization of EVOH, in this invention, 1-20g/EVOH for 10 minutes is preferably used for 2160 g of load, and MFR measured at 210 **. Since the moldability of a constituent needs to worsen and needs to make molding temperature the elevated-temperature side if MFR uses 1g/EVOH for less than 10 minutes, it becomes a cause of a pyrolysis or coloring, and on the other hand, when MFR exceeds 20g/10 minutes, mechanical strength of constituent mold goods becomes dissatisfied.

[0011] Polyamide of this invention is obtained by making polyamide which polymerized by a usual method react to an end blockade agent. Although not limited especially as a method of making an end blockade agent reacting to polyamide, and manufacturing terminal modified

polyamide, a method of adding a terminal modification agent, a method of carrying out melt kneading of the end blockade agent to polyamide resin with an extrusion machine, etc. are used for the polymerization last stage of polyamide resin. Additions of a terminal modification agent are 0.05 - the amount part of duplexes still more preferably 0.02 to 3 weight section preferably 0.01 to 5 weight section to polyamide 100 weight section.

[0012]As polyamide used by this invention, usual polyamide, such as nylon 6, Nylon 66, Nylon 11, Nylon 12, Nylon 610, and Nylon 612, Copolymerization polyamide or such 3 yuan copolymerization polyamide, such as nylon 6 / [nylon 6 /nylon 6/66, nylon 6/12 nylon 6/11, and 6I, Nylon 66 /6I, and] 6T, Nylon 66 /6T, etc. are raised. As for I, isophthalic acid and T show terephthalic acid here.

Desirable one of nylon 6/12 is preferred in respect of nylon 6 and a thickening preventive effect at a cost aspect.

[0013]As carboxylic acid as an end blockade agent, acetic acid, propionic acid, butanoic acid, A valeric acid, caproic acid, enanthic acid, octanoic acid, pelargonic acid, decanoic acid, Dodecanoic acid, lauric acid, myristic acid, pulmitic acid, stearic acid, Behenic acid, montanic acid, oleic acid, linolic acid, benzoic acid, ethylbenzoic acid, Monocarboxylic acid, such as phenylacetic acid, adipic acid, pimelic acid, suberic acid, alpha, such as azelaic acid, sebacic acid, dodecane dione acid, and terephthalic acid, omega-dicarboxylic acid, Hydroxycarboxylic acid, such as alpha, such as maleic acid, succinic acid, methylsuccinic acid, itaconic acid, citraconic acid, phthalic acid, and 1,2-cyclohexanedicarboxylic acid, beta-dicarboxylic acid, citrate, malic acid, gluconic acid, and tartaric acid, etc. are raised. Preferably Adipic acid, pimelic acid, suberic acid, azelaic acid, Sebacic acid, dodecane dione acid, terephthalic acid, maleic acid, succinic acid, Preferably to dicarboxylic acid, such as methylsuccinic acid, itaconic acid, citraconic acid, phthalic acid, and 1,2-cyclohexanedicarboxylic acid, and a pan, alpha, such as maleic acid, succinic acid, methylsuccinic acid, itaconic acid, citraconic acid, phthalic acid, and 1,2-cyclohexanedicarboxylic acid, and beta-dicarboxylic acid are raised.

[0014]Similarly, there is no restriction in particular also as carboxylate, and ester of the above-mentioned carboxylic acid, and various alcohol and phenol is used. For example,

butyl stearate, ethyl benzoate, diethyl succinate, diethyl phthalate, etc. are raised.

[0015]In terminal modification polyamide resin of this invention, amino terminal concentration of terminal modification polyamide resin requires that 3.0×10^{-5} Eq/g or less of 2.0×10^{-5} Eq/g or less should be 1.0×10^{-5} Eq/g or less still more preferably preferably. If amino terminal concentration exceeds g in 3.0×10^{-5} Eq /, after mixing with EVOH and considering it as a constituent, when carrying out extrusion molding, a gelling thing is generated, and continuous molding, such as a film and a sheet, becomes difficult.

[0016]a value which measured relative viscosity [etar] of polyamide resin of this invention at concentration of 1%, and temperature of 25 °C among 98% sulfuric acid according to JIS K6810 -- 2.0-7.0 -- it is 2.0-5.0 preferably. Since mechanical strength of a constituent will worsen if relative viscosity is too low, and a moldability will worsen if too conversely high, it is not desirable.

[0017]The mixture ratio of an ethylene-vinylacetate copolymer (a) and the above-mentioned terminal modification polyamide resin (b) is 5-95 / 95 to 5 % of the weight preferably 99 to 1 1-99-% of the weight. Less than 1 % of the weight of polyamide is not enough as ductility, on the other hand, at less than 1 % of the weight, a gas barrier property improved effect does not show up, and EVOH is not preferred.

[0018]A constituent of this invention is fabricated by various mold goods, such as a pellet, a film for food packing, a sheet, and a container, by melt molding. It is usable also as one ingredient of a multilayer film with polyethylene, polypropylene, etc. in a constituent of this invention. As a melt molding method, publicly known molding means, such as extrusion molding, blow molding, and injection molding, are used preferably.

[0019]In a resin composition of this invention, the characteristic in a range which is not spoiled Various kinds of stabilizer, For example, heat-resistant agents, such as a hindered phenol system, an aromatic amine system, and a copper halide system, Publicly known additive agents, such as weathering agents, such as a benzophenone series, a triazole series, an imidazole series, an oxazol system, and a hindered amine system, and an inorganic bulking agent, fire

retardant, paints, a color, lubricant, an antiblocking agent, or various thermoplastics, may be blended.

[0020] This invention is explained in more detail with a below example. This invention is not limited to the following examples, unless the gist is exceeded.

Measurement evaluation of the weighted solidity described in an example and a comparative example was carried out by a method described below.

[0021] (1) An oxygen permeability film was measured under conditions of 20 °C and 100%RH. a unit -- per one sheet -- : -- they are :cc/m² and 24 hr/0.1 mm per cc/m², 24hr, and 0.1 mm in thickness.

[0022] (2) Melt extruding of the thickening gelling characteristic constituent was carried out from an extrusion machine, a 200-micrometer unstretched film was manufactured continuously, and time until a gelling thing appears innumerable in a film after a film production start and film production becomes impossible was measured.

[0023] (3) Terminal-group-concentration measurement amide terminal group concentration dissolved polyamide in phenol, and titrated and asked for it with 0.02N chloride.

[0024] As shown in the manufacture table 1 of terminal modification polyamide resin, the dry blend of the terminal modification agent was carried out to nylon 6 or nylon 6 / 12 (copolymerization ratios 90/10), and chip making was carried out after formation of a kneading strand at kneading temperature of 260 °C with a 40 mmphi single screw extruder which has a vent-port. Relative viscosity of the obtained terminal modification polyamide resin A-G, and J and terminal amino group concentration are shown in Table 1.

[0025]

[Table 1]

表 1

例	A	B	C	D	E	F	G	H	I	J
ポリアミド系	N 6	N 6	N 6	N 6	N 6/12	N 6/12	N 6/12	N 6	N 6/12	N 6
変性剤種	フタル酸	コハク酸	モンタン酸	カサリ酸 アキ	コハク酸	クエン酸	フタル酸 ジエチル	—	—	ステアリン酸
変性剤量	2.5	2.0	1.0	1.5	0.5	0.2	1.0	—	—	0.1
[η]	2.2	2.5	2.5	2.6	2.9	2.8	3.2	2.8	3.4	2.4
末端アミノ基 μ当量/g	8	9	15	18	25	28	12	55	40	35

[0026]nylon 6 (polyamide C) which carried out terminal modification with Example 1 - 3 succinic acid -- and, After blending an ethylene-vinylacetate copolymer partial

saponification thing (99% of the degree of ethylene content % and saponification of 32 mol, 210 **, MFR3.3g in 2160 g of load/10 minutes) by composition ratio shown in Table 2, with a 40 mmphi single screw extruder, melt kneading was carried out and chip making was carried out. Melt viscosity at the time of 10 minutes [in / for an obtained chip / after vacuum drying and with a melt indexer / 230 **] and 120-minute stagnation (mua) (10 sec of shear rate-1) was measured. A result is shown in Table 2. A thickening degree of the 10-minute back of melting stagnation and 120 minutes after is small, and mixing of a gelling thing was not accepted, either.

[0027]Next, melt extruding of the class product was carried out at 230 ** from the 40 mmphi extrusion machine, and the 200-micro-thick unstretched film was produced continuously. Also in the continuous molding of 24 hours or more, mixing of the gelling thing was not looked at by the film, but the film which was excellent in strange planarity, transparency, and gas barrier property was obtained.

[0028]

[Table 2]

	実施例										比較例		
	1	2	3	4	5	6	7	8	9	10	1	2	3
ポリアミド	B	B	B	A	C	D	E	E	F	G	H	I	J
ナイロン/EVOH	4/6	2/8	1/9	4/6	4/6	4/6	4/6	2/8	4/6	4/6	4/6	4/6	4/6
μ s 10分	9,400	11,400	12,400	9,800	11,800	10,400	11,800	13,900	11,900	9,900	16,200	13,000	12,300
120分	50,500	62,200	81,100	48,800	85,400	71,500	86,600	89,100	95,100	98,500	ゲル化	ゲル化	ゲル化
連続試験時間 hr	>24	>24	>24	>24	>24	>24	>24	>24	>24	>24	4	5	10
融解発熱性													
シート当り 0.1mm 当り	16.0 2.9	9.5 1.8	7.1 1.5	17.0 3.2	15.3 2.9	15.9 2.9	23.0 4.5	22.5 4.3	22.5 4.3	22.8 4.1	—	—	—
ce/m ² .24hr													

[0029]When the kind of four to example 10 nylon and the kind of denaturing agent were changed and constituent-izing

and characterization were performed like Examples 1-3, all were excellent in stagnation stability, continuation film production nature, transparency, and gas barrier property. [0030]EVOH was blended with nylon 6[2 end nylon 6 which is not denaturalized / the comparative example 1 and / and (polyamide H), and] 12 (polyamide I) by the composition ratio of nylon/EVOH=4/6, it constituent-ized like Examples 1-3, and characterization was performed. By the stagnation for 120 minutes, all caused gelling and it became impossible also in continuation film shaping producing a film them by gelling in about 5 hours and 7 hours, respectively.

[0031]EVOH was blended with comparative example 3 terminal-modification nylon 6 (polyamide J) by the composition ratio of nylon/EVOH=4/6, it constituent-ized like Examples 1-3, and characterization was performed. By the stagnation for 120 minutes, gelling was caused and it became impossible also in continuation film shaping producing a film by gelling in about 10 hours.

[0032]

[Effect of the Invention]The continuous fabrication of practical use products, such as a film, a sheet, and a tube, of the resin composition of this invention becomes fusion stability is good and possible.

[Translation done.]